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Fuel and lubricant additive concentrates comprising at least one anthraquinone derivative as a marker

#### Description

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The present invention relates to fuel and lubricant additive concentrates which comprise at least one anthraquinone derivative as a marker, to the use of such concentrates for additizing mineral oils, and also to mineral oils which comprise such concentrates.

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For mineral oil additization, additive concentrates (also referred to herein below, following the relevant terminology, as packages) are used which, in addition to a carrier oil and a mixture of different fuel additives, generally also comprise dyes and also, for invisible fiscal or manufacturer-specific marking, additionally markers. These packages enable the supply of different mineral oil distributors from a pool of unadditized mineral oil, to which the company-specific additization, color and marker are imparted only, for example, while the mineral oil is being filled into appropriate transport containers, with the aid of their individual packages.

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20 The markers are usually substances which are either extracted from the mineral oil and subsequently converted to colored compounds by derivatization, or substances which exhibit absorption either in the visible or in the invisible wavelength region of the spectrum (for example in the NIR). Markers which have been proposed and find use per se, i.e. not just after preceding derivatization, include highly differing compound classes, for example phthalocyanines, naphthalocyanines, nickel-dithiolene complexes, aminium compounds of aromatic amines, methine dyes and azulenesquaric acid dyes (for example WO 94/02570 A1, WO 96/10620 A1), but also bisazo dyes (for example EP 256 460 A1). Anthraquinone derivatives for coloring gasoline or mineral oils are described in the documents US 2,611,772, US 2,068,372, EP 1 001 003 A1 and

30 EP 1 323 811 A2.

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Experience has shown that many of the current markers are stable under the dilute conditions in the mineral oil, but not under the concentrated conditions in the packages; the action of the package components changes the characteristics (e.g. extinction) of the markers within a very short time.

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It is thus an object of the present invention to provide fuel and lubricant additive concentrates which feature very good long-term storage stability, especially also with regard to the stability of the markers present therein against the action of the remaining components of these concentrates.

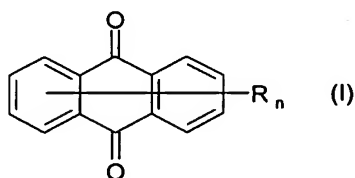
Accordingly, the fuel and lubricant additive concentrates (packages) mentioned at the outset have been found, which comprise at least one anthraquinone derivative as a marker.

5 The components of the inventive packages are in particular:

- a) at least one anthraquinone derivative,
- b) at least one carrier oil,
- c) at least one additive selected from the group consisting of  
10 detergents,  
dispersants and  
valve seat wear-inhibiting additives,
- d) and also, if appropriate, further additives and assistants.

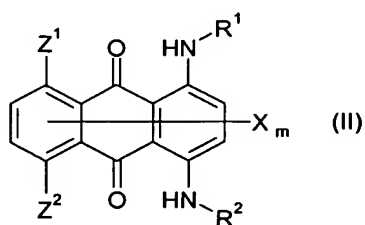
15 The component a) used is in particular anthraquinone derivatives which are selected from the group consisting of the compounds

of the formula I



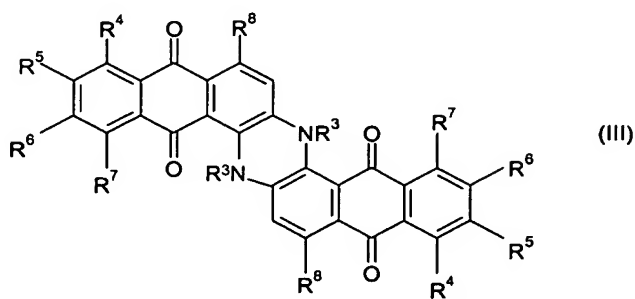
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of the formula II



and of the formula III

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where

- 5  $Z^1, Z^2$  are each independently hydrogen, hydroxyl, OR, NHR or  $NR_2$ ,
- $R^1, R^2$  are each independently R or COR,
- X is hydrogen, cyano, nitro, hydroxyl, OR, amino, NHR, R or  $CH(R^9)(R^{10})$ ,
- 10 n, m are each 0, 1, 2, 3 or 4, and, in each case that n or m is greater than 1, the R or X radicals may each be the same or different,
- $R^9, R^{10}$  are each independently cyano, COOH or COOR,
- 15  $R^3$  is hydrogen, R or NHR,
- $R^4$  to  $R^8$  are each independently hydrogen, R or NHR
- and
- 20 R is  $C_1$ - $C_{20}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_5$ - $C_7$ -cycloalkyl which is optionally substituted by one or more  $C_1$ - $C_{20}$ -alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, saturated heterocyclic five- or six-
- 25 membered radical which is optionally substituted by one or more  $C_1$ - $C_{20}$ -alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, or is  $C_6$ - $C_{10}$ -aryl which is optionally substituted by one or more halogen, cyano, nitro, hydroxyl, amino,  $C_1$ - $C_{20}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{20}$ -alkoxy,  $C_1$ - $C_{20}$ -alkylamino or  $C_1$ - $C_{20}$ -dialkylamino, or is heteroaryl having from 3 to 12 carbon atoms which is optionally substituted by one or more  $C_1$ - $C_{20}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{20}$ -alkoxy,  $C_1$ - $C_{20}$ -alkylamino or  $C_1$ - $C_{20}$ -dialkylamino, or is  $C_6$ - $C_{10}$ -aryl- $C_1$ - $C_4$ -alkyl which is optionally substituted in the aryl radical by one
- 30 or more halogen, cyano, nitro, hydroxyl, amino,  $C_1$ - $C_{20}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{20}$ -alkoxy,  $C_1$ - $C_{20}$ -alkylamino or  $C_1$ - $C_{20}$ -dialkylamino, or is heteroaryl- $C_1$ - $C_4$ -alkyl having from 3 to 12 carbon atoms in the heteroaryl radical, the latter optionally being substituted by one or more  $C_1$ - $C_{20}$ -alkyl which is optionally
- 35

interrupted by from 1 to 4 oxygen atoms in ether function, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkylamino or C<sub>1</sub>-C<sub>20</sub>-dialkylamino.

C<sub>1</sub>-C<sub>20</sub>-Alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function include, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, hept-3-yl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl (the above terms isooctyl, isononyl, isodecyl and isotridecyl are trivial names and stem from the alcohols obtained by the  
 10 oxo process – on this subject, cf. Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Volume 7, pages 215 to 217, and also Volume 11, pages 435 and 436), tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, methoxymethyl, 2-ethylhexoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- or 3-methoxypropyl, 2- or 3-ethoxypropyl, 2- or 3-  
 15 propoxypropyl, 2- or 3-butoxypropyl, 2- or 4-methoxybutyl, 2- or 4-ethoxybutyl, 2- or 4-propoxybutyl, 2- or 4-butoxybutyl, 3,6-dioxahexyl, 3,6-dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl or 3,6,9,12-tetraoxatetradecyl.

20 Useful C<sub>5</sub>-C<sub>7</sub>-cycloalkyl radicals include cyclopentyl, cyclohexyl and cycloheptyl. These cycloalkyls are optionally substituted by one or more, in particular up to three, C<sub>1</sub>-C<sub>20</sub>-alkyl groups, and the latter may optionally be interrupted by from 1 to 4 oxygen atoms in ether function. Examples of such C<sub>1</sub>-C<sub>20</sub>-alkyl groups optionally interrupted by  
 25 oxygen atoms have already been listed above.

Saturated, heterocyclic five- or six-membered radicals which are optionally substituted by one or more C<sub>1</sub>-C<sub>20</sub>-alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function are derived, for example, from pyrrolidine, 2- or 3-  
 30 methylpyrrolidine, 2,4-dimethyl-3-ethylpyrrolidine, pyrazolidine, 2-, 3-, 4- or 5-methylpyrazolidine, imidazolidine, 2-, 3-, 4- or 5-methylimidazolidine, oxazolidine, 2-, 4- or 5-methyloxazolidine, isoxazolidine, 3-, 4- or 5-methylisoxazolidine, piperidine, 2-, 3-, 4-methyl- or -ethylpiperidine, 2,6-dimethylpiperidine, piperazine, 4-(C<sub>1</sub>-C<sub>4</sub>-alkyl)piperazine such as 4-methyl- or 4-ethylpiperazine, morpholine, thiomorpholine or  
 35 thiomorpholine S,S-dioxide.

When R, in the OR, NHR and NR<sub>2</sub> groups of the definition of the variables Z<sup>1</sup> and/or Z<sup>2</sup>, in the OR and NHR groups of the definition of the variables X, in the COOR group of the definition of the R<sup>9</sup> and R<sup>10</sup> radicals, in the NHR group of the definition of the  
 40 variables R<sup>3</sup> and also R<sup>4</sup> to R<sup>8</sup>, corresponds to an appropriate, optionally substituted,

saturated, heterocyclic five- or six-membered radical, it is bonded to the particular heteroatom of the group in question via a carbon atom of the heterocyclic five- or six-membered ring. The same applies when R alone in the definition of the variables  $R^1$  and  $R^2$  and the definition of the variables  $R^3$  corresponds to an appropriate, optionally substituted, saturated, heterocyclic five- or six-membered radical. In the other cases, the bonding may either be via a carbon atom or a heteroatom of the heterocyclic five- or six-membered radical which are suitable for bonding.

$C_6$ - $C_{10}$ -Aryls include in particular phenyl and naphthyl. These are optionally substituted by one or more halogen such as fluorine, chlorine or bromine, cyano, nitro, hydroxyl, amino,  $C_1$ - $C_{20}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{20}$ -alkoxy,  $C_1$ - $C_{20}$ -alkylamino or  $C_1$ - $C_{20}$ -dialkylamino. Appropriate  $C_1$ - $C_{20}$ -alkyl radicals which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, and  $C_1$ - $C_{20}$ -alkyl radicals which are present in the  $C_1$ - $C_{20}$ -alkoxy,  $C_1$ - $C_{20}$ -alkylamino or  $C_1$ - $C_{20}$ -dialkylamino groups have already been listed above by way of example.

Heteroaryl radicals having from 3 to 12 carbon atoms which are optionally substituted by one or more  $C_1$ - $C_{20}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{20}$ -alkoxy,  $C_1$ - $C_{20}$ -alkylamino or  $C_1$ - $C_{20}$ -dialkylamino are derived, for example, from pyrrole, furan, thiophene, pyrazole, isoxazole, isothiazole, imidazole, 1H-1,2,3-triazole, 1H-1,2,4-triazole, pyridine, pyrazine, pyridazine, 1H-azepine, 2H-azepine, oxazole, thiazole, 1,2,3-, 1,2,4- or 1,3,4-oxadiazole, 1,2,3-, 1,2,4- or 1,3,4-thiadiazole and also optionally the benzo or dibenzofused rings, for example quinoline, isoquinoline, indole, benzo[b]furan (coumarone), benzo[b]thiophene (thionaphthene), carbazole, dibenzofuran, dibenzothiophene, 1H-indazole, indoxazole, benzo[d]isothiazole, anthranil, benzimidazole, benzoxazole, benzothiazole, cinnoline, phthalazine, quinazoline, quinoxaline or phenazine.  $C_1$ - $C_{20}$ -Alkyl substituents which are optionally interrupted by from 1 to 4 oxygen atoms in ether function have already been specified above by way of example.

When R, in the OR, NHR and  $NR_2$  groups of the definition of the variables  $Z^1$  and/or  $Z^2$ , in the OR and NHR groups of the definition of the variables X, in the COOR group of the definition of the  $R^9$  and  $R^{10}$  radicals, in the NHR group of the definition of the variables  $R^3$  and also  $R^4$  to  $R^8$ , corresponds to an appropriate, optionally substituted heteroaryl, it is bonded to the particular heteroatom of the group in question via a carbon atom of the heteroaryl. The same applies when R alone in the definition of the variables  $R^1$  and/or  $R^2$  and the definition of the variables  $R^3$  corresponds to an appropriate, optionally substituted heteroaryl. In the other cases, the bonding may

either be via a carbon atom or a heteroatom of the heteroaryl which is suitable for bonding.

5 C<sub>6</sub>-C<sub>10</sub>-Aryl-C<sub>1</sub>-C<sub>4</sub>-alkyls which are optionally substituted in the aryl radical by one or more halogen, cyano, nitro, hydroxyl, amino, C<sub>1</sub>-C<sub>20</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkylamino or C<sub>1</sub>-C<sub>20</sub>-dialkylamino include in particular benzyl, phenylethyl, 3-phenylpropyl and 4-phenylbutyl. Appropriate C<sub>1</sub>-C<sub>20</sub>-alkyl radicals which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, and C<sub>1</sub>-C<sub>20</sub>-alkyl radicals which are present in the  
10 C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkylamino or C<sub>1</sub>-C<sub>20</sub>-dialkylamino groups have already been listed above by way of example.

Heteroaryl-C<sub>1</sub>-C<sub>4</sub>-alkyls having from 3 to 12 carbon atoms in the heteroaryl radical, the latter optionally being substituted by one or more C<sub>1</sub>-C<sub>20</sub>-alkyl which is optionally  
15 interrupted by from 1 to 4 oxygen atoms in ether function, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkylamino or C<sub>1</sub>-C<sub>20</sub>-dialkylamino are derived, for example, from the heteroaryl radicals specified above which are bonded to the C<sub>1</sub>-C<sub>4</sub>-alkyl radicals either via a carbon atom or a heteroatom of the heteroaryl which is suitable for bonding. Appropriate C<sub>1</sub>-C<sub>20</sub>-alkyl radicals which are optionally interrupted by from 1 to 4 oxygen atoms in ether function,  
20 and C<sub>1</sub>-C<sub>20</sub>-alkyl radicals which are present in the C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkylamino or C<sub>1</sub>-C<sub>20</sub>-dialkylamino groups have already been listed above by way of example.

Preferred inventive fuel and lubricant additive concentrates comprise anthraquinone derivatives of the formulae I, II and III where

25 Z<sup>1</sup>, Z<sup>2</sup> are each independently hydrogen or NHR,

R<sup>1</sup>, R<sup>2</sup> are each independently R,

30 X is hydrogen, cyano or CH(R<sup>9</sup>)(R<sup>10</sup>),

n, m are 0, 1, 2, 3 or 4, and, when n or m is greater than 1, the R or X radicals are the same or different,

35 R<sup>9</sup>, R<sup>10</sup> are each independently cyano or COOR,

R<sup>3</sup> is hydrogen, R or NHR,

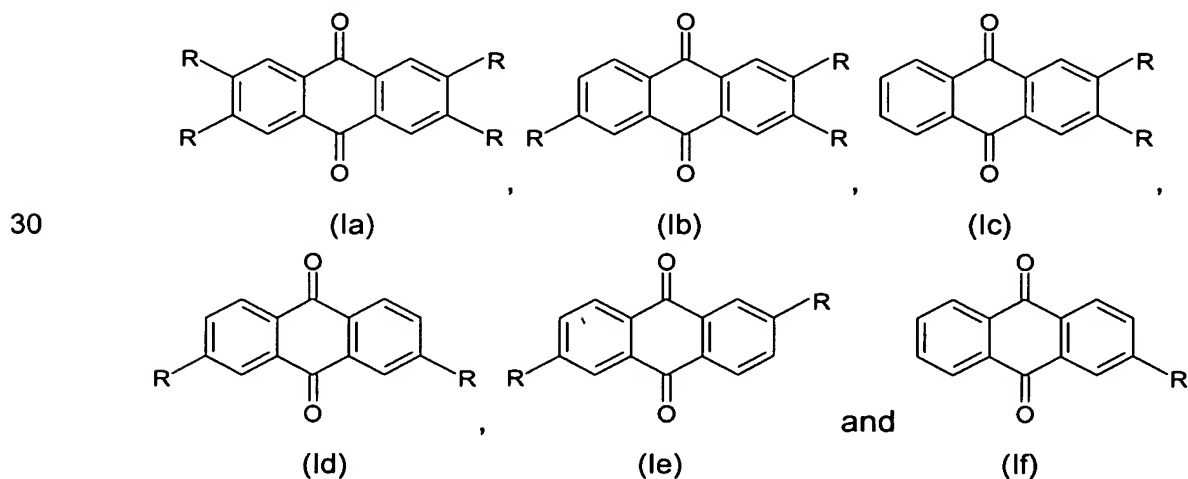
R<sup>4</sup> to R<sup>7</sup> are hydrogen or NHR,  
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$R^8$  is NHR

and

- 5 R is  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, cyclohexyl which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, saturated heterocyclic five- or six-membered radical which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, or is
- 10  $C_6$ - $C_{10}$ -aryl which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{15}$ -alkoxy,  $C_1$ - $C_{15}$ -alkylamino or  $C_1$ - $C_{15}$ -dialkylamino, or is heteroaryl having from 3 to 5 carbon atoms which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{15}$ -alkoxy,  $C_1$ - $C_{15}$ -alkylamino or  $C_1$ - $C_{15}$ -dialkylamino, or is
- 15 phenyl  $C_1$ - $C_4$ -alkyl which is optionally substituted in the phenyl radical by one or more  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{15}$ -alkoxy,  $C_1$ - $C_{15}$ -alkylamino or  $C_1$ - $C_{15}$ -dialkylamino, or is heteroaryl- $C_1$ - $C_4$ -alkyl having from 3 to 5 carbon atoms in the heteroaryl radical, the latter optionally being substituted by one or more  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{15}$ -alkoxy,  $C_1$ - $C_{15}$ -alkylamino or  $C_1$ - $C_{15}$ -dialkylamino,
- 20
- 25 the preferred R radicals already having been listed in the above exemplary list.

Anthraquinone derivatives of the formula I are in particular the compounds of the formulae Ia to If shown below:



In the formulae Ia to Ie, the variables R are in each case independently, and in formula If the variable R is, C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, and C<sub>6</sub>-C<sub>10</sub>-aryl which is optionally substituted by one or more

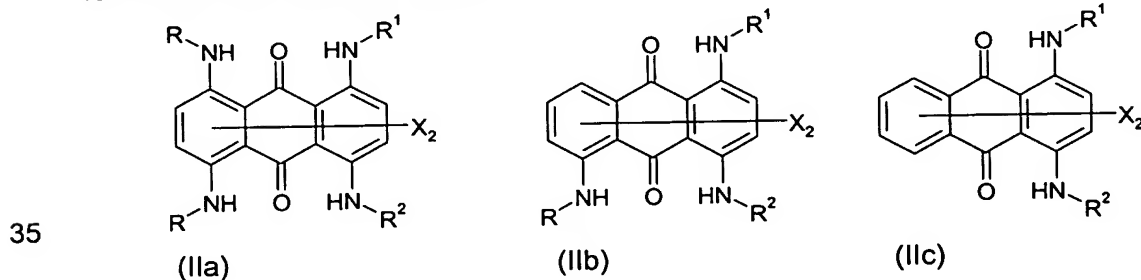
5 C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function.

In the definition of a C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally substituted by from 1 to 4 oxygen atoms in ether function, the variables R are preferably selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, hept-3-yl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl, tetradecyl, pentadecyl, methoxymethyl, 2-ethylhexoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- and 3-methoxypropyl, 2- and 3-ethoxypropyl, 2- and 3-propoxypropyl, 2- and 3-butoxypropyl, 2- and 4-methoxybutyl, 2- and 4-ethoxybutyl, 2- and 4-propoxybutyl, 2- and 4-butoxybutyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl and 3,6,9,12-tetraoxatetradecyl.

In the definition of a C<sub>6</sub>-C<sub>10</sub>-aryl which is optionally substituted by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, the variables R are preferably selected from the group consisting of unsubstituted phenyl, the 2-, 3- and 4-monosubstituted, the 2,3-, 2,4- and 3,4-disubstituted and the 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- and 3,4,5-trisubstituted phenyl radicals which are substituted by the C<sub>1</sub>-C<sub>15</sub>-alkyl radicals which are optionally interrupted by oxygen in ether function and have been listed above by way of example.

30 The particular R radicals in the compounds of the formulae Ia to Ie are preferably the same.

Anthraquinone derivatives of the formula II are in particular the compounds of the formulae IIa to IIc shown below:





In the formulae IIa to IIc, the variables R, R<sup>1</sup> and R<sup>2</sup> are each independently C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, and C<sub>6</sub>-C<sub>10</sub>-aryl which is optionally substituted by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function.

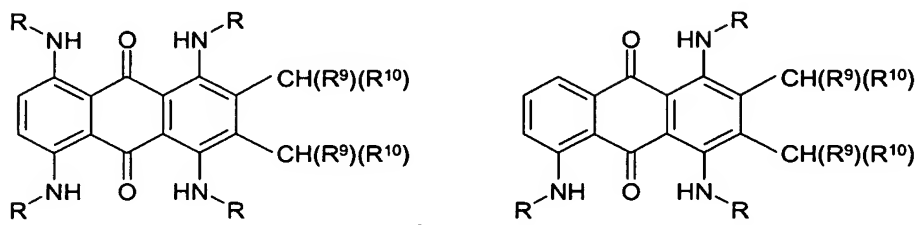
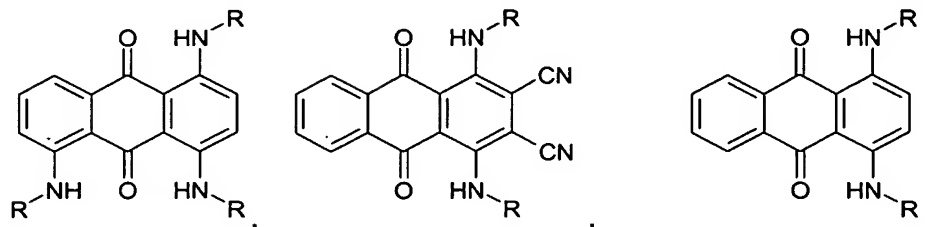
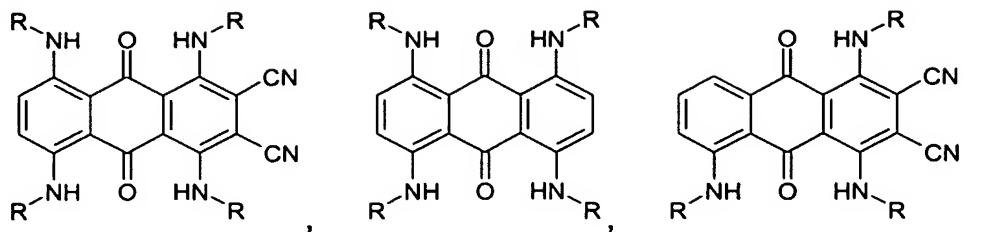
X in the formulae IIa to IIc either takes the meaning of two hydrogen atoms, two cyano groups in the 2,3- or 6,7-arrangement or two identical CH(R<sup>9</sup>)(R<sup>10</sup>) groups in the 2,3- or 6,7-arrangement of the anthraquinone structure. The latter two CH(R<sup>9</sup>)(R<sup>10</sup>) groups are either two CH(COOR)<sub>2</sub>, CH(CN)COOR or CH(CN)<sub>2</sub> groups, where the R radicals are preferably C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, or C<sub>6</sub>-C<sub>10</sub>-aryl which is optionally substituted by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function.

In the definition of a C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, the variables R, R<sup>1</sup> and R<sup>2</sup> are preferably selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, hept-3-yl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl, tetradecyl, pentadecyl, methoxymethyl, 2-ethylhexoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- and 3-methoxypropyl, 2- and 3-ethoxypropyl, 2- and 3-propoxypropyl, 2- and 3-butoxypropyl, 2- and 4-methoxybutyl, 2- and 4-ethoxybutyl, 2- and 4-propoxybutyl, 2- and 4-butoxybutyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl and 3,6,9,12-tetraoxatetradecyl.

In the definition of a C<sub>6</sub>-C<sub>10</sub>-aryl which is optionally substituted by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, the variables R, R<sup>1</sup> and R<sup>2</sup> are preferably selected from the group consisting of unsubstituted phenyl, the 2-, 3- and 4-monosubstituted, 2,3-, 2,4- and 3,4-disubstituted and the 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- and 3,4,5-trisubstituted phenyl radicals which are substituted by the C<sub>1</sub>-C<sub>15</sub>-alkyl radicals which are optionally interrupted by oxygen in ether function and are listed above by way of example.

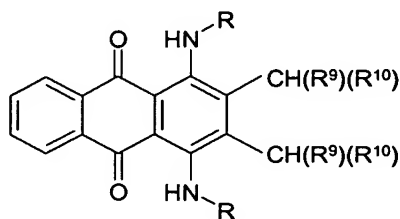
Particular preference is given to compounds of the formulae IIa, IIb and IIc in which both variables R, R<sup>1</sup> and R<sup>2</sup>, or R, R<sup>1</sup> and R<sup>2</sup>, or R<sup>1</sup> and R<sup>2</sup> are the same as one another, i.e. corresponding compounds include:

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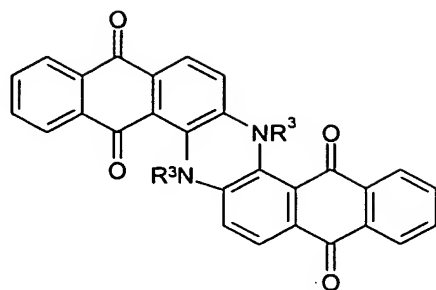
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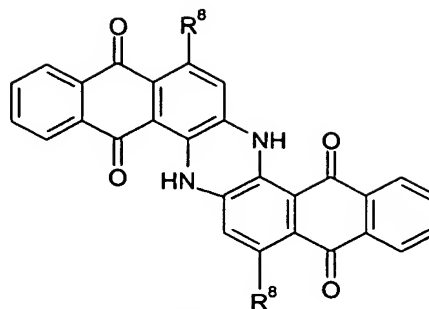


and also the corresponding compounds 6,7-substituted by cyano groups or  
 10  $\text{CH(R}^9\text{)(R}^{10}\text{)}$  groups, the variables R corresponding to the selections listed above.

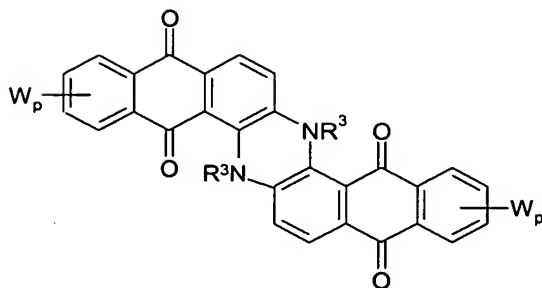
Anthraquinone derivatives of the formula III to be used in accordance with the invention are in particular the compounds of the formulae IIIa to IIId shown below:



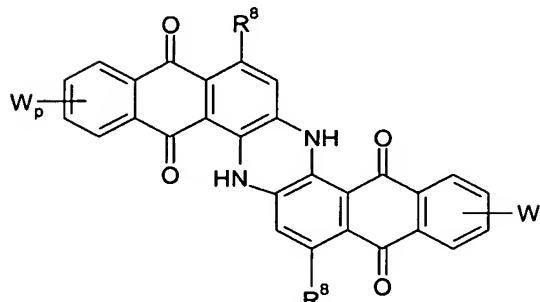
(IIIa)



(IIIb)



(IIIc)



(IIId)

where

5

$R^3$  is R or NHR,

$R^8$  is NHR

10  $W$  is  $R^4$  to  $R^7$  radicals in the definition of hydrogen or NHR,

$p$  is 1, 2, 3 or 4, and, when  $p$  is greater than 1, the radicals are the same,

and

15

20  $R$  is  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, cyclohexyl which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, saturated heterocyclic five- or six-membered radical which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl groups which are optionally interrupted by from 1 to 4 oxygen atoms in ether function, or is  $C_6$ - $C_{10}$ -aryl which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{15}$ -alkoxy,  $C_1$ - $C_{15}$ -alkylamino or  $C_1$ - $C_{15}$ -dialkylamino, or is heteroaryl having from 3 to 5 carbon atoms which is optionally substituted by one or more  $C_1$ - $C_{15}$ -alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function,  $C_1$ - $C_{15}$ -

25

alkoxy, C<sub>1</sub>-C<sub>15</sub>-alkylamino or C<sub>1</sub>-C<sub>15</sub>-dialkylamino, or is phenyl C<sub>1</sub>-C<sub>4</sub>-alkyl which is optionally substituted in the phenyl radical by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, C<sub>1</sub>-C<sub>15</sub>-alkoxy, C<sub>1</sub>-C<sub>15</sub>-alkylamino or C<sub>1</sub>-C<sub>15</sub>-dialkylamino, or is heteroaryl-C<sub>1</sub>-C<sub>4</sub>-alkyl having from 3 to 5 carbon atoms in the heteroaryl radical, the latter optionally being substituted by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, C<sub>1</sub>-C<sub>15</sub>-alkoxy, C<sub>1</sub>-C<sub>15</sub>-alkylamino or C<sub>1</sub>-C<sub>15</sub>-dialkylamino,

the preferred R radicals already having been listed by way of example in the above-described general definition of the R radicals.

R in the formulae IIIa to IIId is more preferably C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function, or C<sub>6</sub>-C<sub>10</sub>-aryl which is optionally interrupted by one or more C<sub>1</sub>-C<sub>15</sub>-alkyl which is optionally interrupted by from 1 to 4 oxygen atoms in ether function.

In particular, R in the formulae IIIa to IIId is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, hept-3-yl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl, tetradecyl, pentadecyl, methoxymethyl, 2-ethylhexoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- and 3-methoxypropyl, 2- and 3-ethoxypropyl, 2- and 3-propoxypropyl, 2- and 3-butoxypropyl, 2- and 4-methoxybutyl, 2- and 4-ethoxybutyl, 2- and 4-propoxybutyl, 2- and 4-butoxybutyl, 3,6-dioxahexyl, 3,6-dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl, 3,6,9,12-tetraoxatetradecyl, unsubstituted phenyl, the 2-, 3- and 4-monosubstituted, the 2,3-, 2,4- and 3,4-disubstituted and the 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- and 3,4,5-trisubstituted phenyl radicals which are substituted by the C<sub>1</sub>-C<sub>15</sub>-alkyl radicals which are optionally interrupted by oxygen in ether function and have been listed above by way of example, selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, hept-3-yl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl, tetradecyl, pentadecyl, methoxymethyl, 2-ethylhexoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- and 3-methoxypropyl, 2- and 3-ethoxypropyl, 2- and 3-propoxypropyl, 2- and 3-butoxypropyl, 2- and 4-methoxybutyl, 2- and 4-ethoxybutyl, 2- and 4-propoxybutyl, 2- and 4-butoxybutyl, 3,6-dioxahexyl, 3,6-

dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl and 3,6,9,12-tetraoxatetradecyl.

- 5 The carrier oils used are typically viscous, high-boiling and in particular thermally stable liquids. They cover the hot metal surfaces, for example the intake valves, with a thin liquid film and thus prevent or delay the formation and deposition of decomposition products on the metal surfaces.
- 10 Carrier oils useful as component b) of the inventive fuel and lubricant additive concentrates are, for example, mineral carrier oils (base oils), especially those of the Solvent Neutral (SN) 500 to 2000 viscosity class, synthetic carrier oils based on olefin polymers having  $M_N$  = from 400 to 1800, in particular based on polybutene or polyisobutene (hydrogenated or nonhydrogenated), on poly- $\alpha$ -olefins or
- 15 poly(internal olefins) and also synthetic carrier oils based on alkoxylated long-chain alcohols or phenols. According to the invention, adducts, to be used as carrier oils, of ethylene oxide, propylene oxide and/or butylene oxide to polybutyl alcohols or polyisobutene alcohols are described for instance, in EP 277 345 A1; further polyalkene alcohol polyalkoxylates to be used in accordance with the invention are
- 20 described in WO 00/50543 A1. Further carrier oils to be used in accordance with the invention also include polyalkene alcohol polyether amines, as detailed in WO 00/61708.

It will be appreciated that mixtures of different carrier oils may also be used, as long as

25 they are compatible with one another and with the remaining components of the inventive packages.

Carburetors and intake systems of internal combustion engines, but also injection systems for fuel metering, are being contaminated to an increasing degree by

30 impurities which are caused, for example, by dust particles from the air and uncombusted hydrocarbons from the combustion chamber.

To reduce or prevent these contaminations, additives ("detergents") are added to the fuel to keep valves and carburetors or injection systems clean. Such detergents are

35 generally used in combination with one or more carrier oils. The carrier oils exert an additional "wash function", support and often promote the detergents in their action of cleaning and keeping clean, and can thus contribute to the reduction in the amount of detergents required.

It should also be mentioned here that many of the substances typically used as carrier oils display additional action as detergents and/or dispersants, which is why the proportion of the latter can be reduced in such a case. Such carrier oils having detergent/dispersant action are detailed, for instance, in the last-mentioned WO document.

It is also often impossible to clearly delimit the mode of action of detergents, dispersants and valve seat wear-inhibiting additives, which is why these compounds are listed in summary under component c). Customary detergents which find use in the inventive packages are listed, for example, in WO 00/50543 A1 and WO 00/61708 A1 and include:

Polyisobutenamines which are obtainable according to EP-A 244 616 by hydroformylation of highly reactive polyisobutene and subsequent reductive amination with ammonia, monoamines or polyamines, such as dimethylenaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine,

Poly(iso)butenamines which are obtainable by chlorination of polybutenes or polyisobutenes having double bonds predominantly in the b- and g-position and subsequent amination with ammonia, monoamines or the abovementioned polyamines,

Poly(iso)butenamines which are obtainable by oxidation of double bonds in poly(iso)butenes with air or ozone to give carbonyl or carboxyl compounds and subsequent amination under reducing (hydrogenating) conditions,

Polyisobutenamines which are obtainable according to DE-A 196 20 262 from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols,

Polyisobutenamines which optionally contain hydroxyl groups and are obtainable according to WO-A 97/03946 by reaction of polyisobutenes having an average degree of polymerization P of from 5 to 100 with oxides of nitrogen or mixtures of oxides of nitrogen and oxygen and subsequent hydrogenation of these reaction products,

Hydroxyl-containing polyisobutenamines which are obtainable according to EP-A 476 485 by reaction of polyisobutene epoxides with ammonia, monoamines or the abovementioned polyamines,

5 Polyetheramines which are obtainable by reaction of C<sub>2</sub>- to C<sub>30</sub>-alkanols, C<sub>6</sub>- to C<sub>30</sub>-alkanediols, mono- or di-C<sub>2</sub>- to C<sub>30</sub>-alkylamines, C<sub>1</sub>- to C<sub>30</sub>-alkylcyclohexanols or C<sub>1</sub>- to C<sub>30</sub>-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl or amino group and subsequent reductive amination with ammonia, monoamines or the abovementioned polyamines, and also

10 "Polyisobutene Mannich bases" which are obtainable according to EP-A 831 141 by reaction of polyisobutene-substituted phenols with aldehydes and monoamines or the abovementioned polyamines.

15 Further detergents and/or valve seat wear-inhibiting additives to be used in accordance with the invention are listed, for example, in WO 00/47698 A1 and include compounds which have at least one hydrophobic hydrocarbon radical having a number-average molecular weight ( $M_N$ ) of from 85 to 20 000 and at least one polar moiety, and which are selected from:

- 20 (i) mono- or polyamino groups having up to 6 nitrogen atoms, of which at least one nitrogen atom has basic properties;
- (ii) nitro groups, optionally in combination with hydroxyl groups;
- (iii) hydroxyl groups in combination with mono- or polyamino groups, in which at least  
25 one nitrogen atom has basic properties;
- (iv) carboxyl groups or their alkali metal or their alkaline earth metal salts;
- (v) sulfonic acid groups or their alkali metal or alkaline earth metal salts;  
30
- (vi) polyoxy-C<sub>2</sub>- to -C<sub>4</sub>-alkylene groups which are terminated by hydroxyl groups, mono- or polyamino groups, in which at least one nitrogen atom has basic properties, or by carbamate groups;
- 35 (vii) carboxylic ester groups;

(viii) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or

5 (ix) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

Additives containing mono- or polyamino groups (i) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or on highly reactive (i.e. having predominantly terminal double bonds, usually in the  $\beta$ - and  $\gamma$ -positions) or conventional  
10 (i.e. having predominantly internal double bonds) polybutene or polyisobutene having  $M_N$  = from 300 to 5000. Such additives based on highly reactive polyisobutene, which can be prepared from the polyisobutene (which may contain up to 20% by weight of n-butene units) by hydroformylation and reductive amination with ammonia, monoamines or polyamines, such as dimethylaminopropylamine, ethylenediamine,  
15 diethylenetriamine, triethylenetetramine or tetraethylenepentamine, are disclosed in particular in EP 244 616 A2. When polybutene or polyisobutene having predominantly internal double bonds (usually in the  $\beta$ - and  $\gamma$ -positions) are used as starting materials in the preparation of the additives, a possible preparative route is by chlorination and subsequent amination or by oxidation of the double bond with air or ozone to give the  
20 carbonyl or carboxyl compound and subsequent amination under reductive (hydrogenating) conditions. The amines used here for the amination may be the same as those used above for the reductive amination of the hydroformylated highly reactive polyisobutene. Corresponding additives based on polypropene are described in particular in WO 94/24231 A1.

25 Further preferred additives containing monoamino groups (i) are the hydrogenation products of the reaction products of polyisobutenes having an average degree of polymerization  $P$  = from 5 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO 97/03946 A1.

30 Further preferred additives containing monoamino groups (i) are the compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols, as described in particular in DE 196 20 262 A1.

35 Additives containing nitro groups (ii), optionally in combination with hydroxyl groups, are preferably reaction products of polyisobutenes having an average degree of polymerization  $P$  of from 5 to 100 or from 10 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO 96/03367 A1 and



WO 96/03479 A1. These reaction products are generally mixtures of pure nitropolyisobutanes (e.g.  $\alpha,\beta$ -dinitropolyisobutane) and mixed hydroxynitropolyisobutanes (e.g.  $\alpha$ -nitro- $\beta$ -hydroxypolyisobutane).

5 Additives containing hydroxyl groups in combination with mono- or polyamino groups (iii) are in particular reaction products of polyisobutene epoxides obtainable from polyisobutene having preferably predominantly terminal double bonds and  $M_N$  = from 300 to 5000, with ammonia or mono- or polyamines, as described in particular in EP 476 485 A1.

10

Additives containing carboxyl groups or their alkali metal or alkaline earth metal salts (iv) are preferably copolymers of  $C_2$ - $C_{40}$ -olefins with maleic anhydride which have a total molar mass of from 500 to 20 000 and of whose carboxyl groups some or all have been converted to the alkali metal or alkaline earth metal salts and any remainder of the carboxyl groups has been reacted with alcohols or amines. Such additives are disclosed in particular by EP 307 815 A1. Such additives serve mainly to prevent valve seat wear and can, as described in WO 87/01126 A1, advantageously be used in combination with customary detergents such as poly(iso)butenamines or polyetheramines.

20

Additives containing sulfonic acid groups or their alkali metal or alkaline earth metal salts (v) are preferably alkali metal or alkaline earth metal salts of an alkyl sulfosuccinate, as described in particular in EP 639 632 A1. Such additives serve mainly to prevent valve seat wear and can be used advantageously in combination with customary detergents such as poly(iso)butenamines or polyetheramines.

25

Additives containing polyoxy- $C_2$ - $C_4$ -alkylene moieties (vi) are preferably polyethers or polyetheramines which are obtainable by reaction of  $C_2$ - to  $C_{60}$ -alkanols,  $C_6$ - to  $C_{30}$ -alkanediols, mono- or di- $C_2$ - $C_{30}$ -alkylamines,  $C_1$ - $C_{30}$ -alkylcyclohexanols or  $C_1$ - $C_{30}$ -alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of the polyetheramines, by subsequent reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP 310 875 A1, EP 356 725 A1, EP 700 985 A1 and US 4, 877, 416. In the case of polyethers, such products also have carrier oil properties. Typical examples of these are tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and also the corresponding reaction products with ammonia.

35

Additives containing carboxylic ester groups (vii) are preferably esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mm<sup>2</sup>/s at 100°C, as described in particular in DE 38 38 918 A1.

5 The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids, and particularly suitable ester alcohols or ester polyols are long-chain representatives having, for example, from 6 to 24 carbon atoms. Typical representatives of the esters are adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol. Such products also have carrier oil properties.

10

Additives containing moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups (viii) are preferably corresponding derivatives of polyisobutenylsuccinic anhydride which are obtainable by reacting conventional or highly reactive polyisobutene having  $M_N$  = from 300 to 5000 with maleic anhydride by a thermal route or via the chlorinated polyisobutene. Particular interest  
15 attaches to derivatives with aliphatic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. Such gasoline fuel additives are described in particular in US 4, 849, 572.

20 Additives containing moieties obtained by Mannich reaction of phenolic hydroxyl groups with aldehydes and mono- or polyamines (ix) are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and mono- or polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. The polyisobutenyl-substituted phenols may stem from  
25 conventional or highly reactive polyisobutene having  $M_N$  = from 300 to 5000. Such "polyisobutene-Mannich bases" are described in particular in EP 831 141 A1.

For a more precise definition of the additives detailed individually, reference is explicitly made here to the disclosures of the abovementioned prior art documents.

30

Dispersants as component c) are, for example, imides, amides, esters and ammonium and alkali metal salts of polyisobutenesuccinic anhydrides. These compounds find use especially in lubricant oils, but sometimes also as detergents in fuel compositions.

35 Further additives and assistants which may, if desired, be present as component d) of the inventive packages are

organic solvents, for example alcohols such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, pentanol, isopentanol, neopentanol or  
40 hexanol, for example glycols such as 1,2-ethylene glycol, 1,2- or 1,3-propylene glycol,

- 1,2-, 2,3- or 1,4-butylene glycol, di- or triethylene glycol or di- or tripropylene glycol, for example ethers such as methyl tert-butyl ether, 1,2-ethylene glycol monomethyl ether or 1,2-ethylene glycol dimethyl ether, 1,2-ethylene glycol monoethyl ether or 1,2-ethylene glycol diethyl ether, 3-methoxypropanol, 3-isopropoxypropanol,
- 5 tetrahydrofuran or dioxane, for example ketones such as acetone, methyl ethyl ketone or diacetone alcohol, for example esters such as methyl acetate, ethyl acetate, propyl acetate or butyl acetate, for example lactams such as N-methylpyrrolidinone (NMP), for example aliphatic or aromatic hydrocarbons and also mixtures thereof such as
- 10 pentane, hexane, heptane, octane, isooctane, petroleum ether, toluene, xylene, ethylbenzene, tetralin, decalin, dimethylnaphthalene or white spirit and, for example, mineral oil such as gasoline, kerosene, diesel oil or heating oil,
- corrosion inhibitors, for example based on ammonium salts, having a tendency to form films, of organic carboxylic acids or of heterocyclic aromatics in the case of ferrous
- 15 metal corrosion protection,
- antioxidants or stabilizers, for example based on amines such as p-phenylenediamine, dicyclohexylamine or derivatives thereof or on phenols such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid,
- 20 demulsifiers,
- antistats,
- metallocenes such as ferrocene or methylcyclopentadienylmanganese tricarbonyl,
- 25 lubricity improvers (lubricity additives) such as certain fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl) fatty amines, hydroxyacetamides or castor oil,
- amines for reducing the pH of the fuel,
- 30 further markers other than anthraquinone derivatives and
- dyes.
- 35 The concentration of component a), i.e. the at least one anthraquinone derivative, in the inventive packages is typically selected in such a magnitude that, after addition of the package to the mineral oil, the desired concentration of marker(s) is present therein. Typical concentrations of the markers in the mineral oil are, for instance, in the range from 0.01 up to a few 10s of ppm by weight.
- 40

Component b), i.e. the at least one carrier oil, is present in the inventive packages typically in a concentration of from 1 to 50% by weight, in particular from 5 to 30% by weight, and

- 5 component c), i.e. the at least one detergent and/or the at least one dispersant, typically in a concentration of from 25 to 90% by weight, in particular from 30 to 80% by weight,

- 10 based in each case on the total amount of components a) to c) and, where present, d), the sum of the individual concentrations of components a) to c) and, where present d) adding up to 100% by weight.

- 15 When, as component d), corrosion inhibitors, antioxidants or stabilizers, demulsifiers, antistats, metallocenes, lubricity improvers and amines to reduce the pH of the fuel are present in the inventive packages, the sum of their concentrations typically does not exceed 10% by weight, based on the total weight of the package (i.e. the total amount of components a) to c) and d)), the concentration of the corrosion inhibitors and demulsifiers being typically in the range of from in each case about 0.01 to 0.5% by weight of the total amount of the package.

- 20 When, as component d), additional organic solvents (i.e. not already introduced with the remaining components) are present in the inventive packages, the sum of their concentrations typically does not exceed 20% by weight, based on the total amount of the package. These solvents generally stem from solutions of the markers and/or dyes, 25 which are added to the packages instead of the pure markers and/or dyes with a view to more precise meterability.

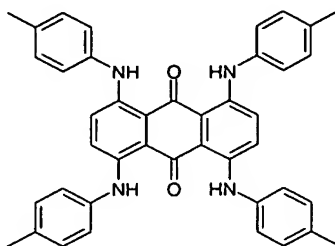
- 30 When, as component d), further markers other than anthraquinone derivatives are present in the inventive packages, their concentration is in turn based on the content that they are to have after addition of the packages in mineral oil. That which was stated for component a) applies mutatis mutandis.

- 35 When, as component d), dyes are present in the inventive packages, their concentration is typically, for instance, between 0.1 to 5% by weight, based on the total amount of the package.

## Examples:

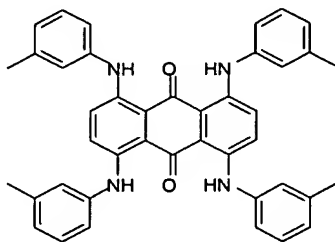
Anthraquinone derivatives shown below were investigated. The compounds 1 to 9 were synthesized starting from 1,4,5,8-tetrachloroanthraquinone and the appropriately substituted anilines by the method described in the document EP 0 323 184 A1.

Compound 1 ( $\lambda_{\text{max}}$  = 753 nm, THF):

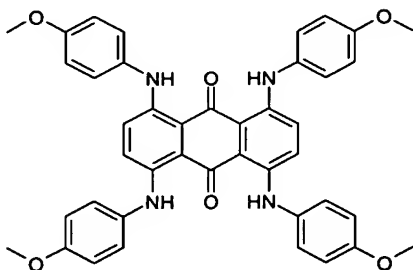


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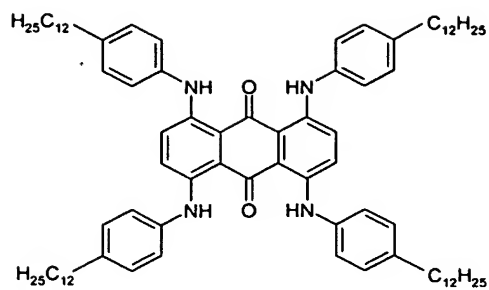
Compound 2 ( $\lambda_{\text{max}}$  = 750 nm, THF):



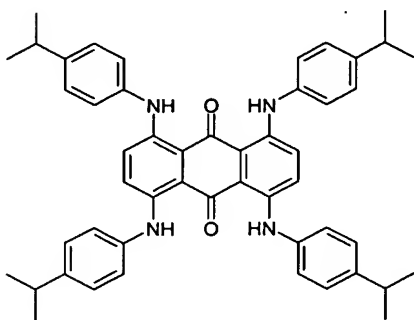
15 Compound 3 ( $\lambda_{\text{max}}$  = 673 nm, THF):



Compound 4 ( $\lambda_{\text{max}}$  = 758 nm, THF):

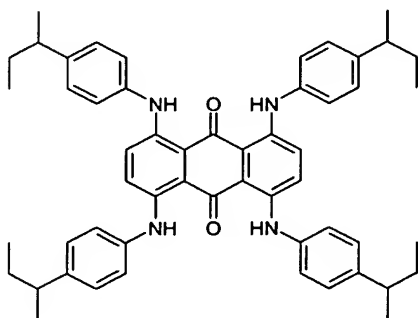


5 Compound 5 ( $\lambda_{\text{max}}$  = 756 nm, THF):

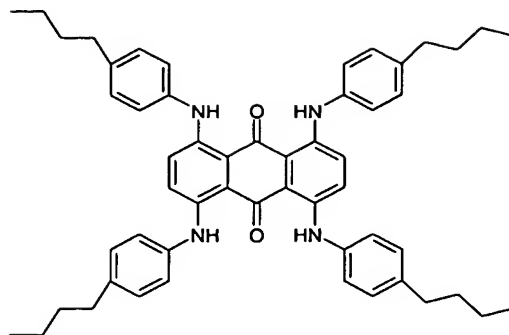


Compound 6 ( $\lambda_{\text{max}}$  = 756 nm, THF):

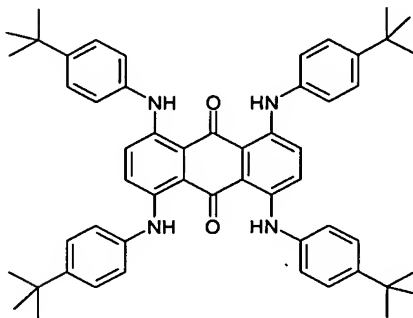
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Compound 7 ( $\lambda_{\text{max}}$  = 756 nm, THF):

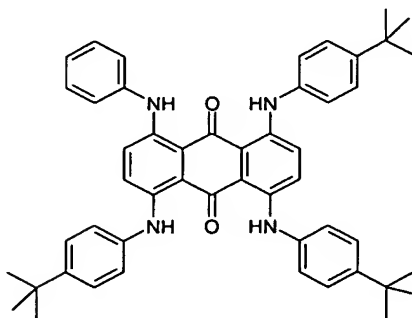


5 Compound 8:



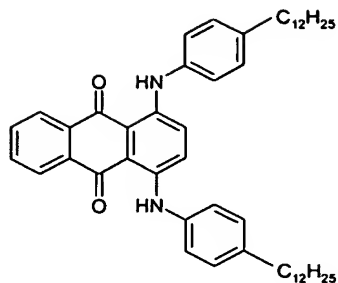
Compound 9 ( $\lambda_{\text{max}}$  = 670 nm, THF):

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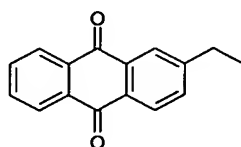
The trisubstituted compound was obtained as a by-product in the preparation of compound 8.

24

Compound 10 ( $\lambda_{\text{max}}$  = 643 nm, THF):

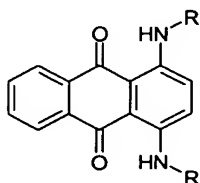
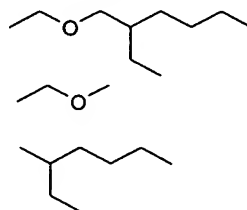
S.G. 33 (commercially available from BASF Aktiengesellschaft)

5

Compound 11 ( $\lambda_{\text{max}}$  = 328 nm, THF):

(commercially available from BASF Aktiengesellschaft)

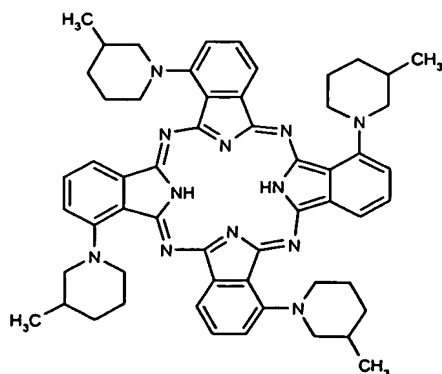
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Compound 12 ( $\lambda_{\text{max}}$  = 648 nm, THF):**R: mixture of the radicals**

S.B. 79 (commercially available from BASF Aktiengesellschaft)

15 Comparison ( $\lambda_{\text{max}}$  = 770 nm, THF):

The comparative compound used was the phthalocyanine of the following formula:





(prepared according to Example 1 of WO 98/52950 A1)

Experiments on storage stability:

- 5 The test mixture used, of a fuel and lubricant additive concentrate with the components contained therein and their particular proportions, is detailed below in Table 1:

Table 1:

Component	Chemical composition	% by weight
Commercial detergent	Polyisobutenamine (PIBA); solution with PIBA content of 50% by weight	70
Commercial carrier oil	Fatty alcohol propoxylate	15
Commercial corrosion protection	Dimerized and oligomerized fatty acids	0.1
Commercial demulsifier	Fatty alcohol ethoxylate	0.1
Solvent	Xylene	14.8

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(Detergent, carrier oil, corrosion protection and demulsifier are commercially available, for example, from or via BASF Aktiengesellschaft)

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- A) The storage stability of compounds 1 to 9 and of the comparative compound compared to the main constituents, detergent and carrier oil, specified in Table 1 was investigated. To this end, from 50 to 100 mg of the particular compound were dissolved in 50 ml of Shellsol AB or, when the solubility of the compound in Shellsol AB was insufficient, it was first incipiently dissolved with approx. 5 ml of isopropanol or NMP and then diluted to 50 ml with Shellsol AB. Subsequently,

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From 1 to 3 ml of the filtrate were diluted to 10 ml with detergent or carrier oil (corresponding to a concentration of the particular compound of from 0.01 to 0.08%) and measured in 1 mm cuvettes against the corresponding unadditized reference.

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The samples were transferred to 10 ml ampules, sealed in an airtight manner and stored in a water bath at 50°C.

The results are reproduced in Tables 2 and 3. All experiments were normalized to the starting extinction.

Table 2: Comparison of the storage stability at 50°C compared to the detergent

Compound	Storage time (h)	Wavelength (nm)	Extinction (normalized)
Comparison	0	768	1.00
	114		0.33
	161		0.20
	283		0.05
1	425		1.00
2	451	752	0.96
3	475	681	0.98
4	500	758	0.86
5	500	756	1.00
6	500	756	0.98
7	500	756	1.00
9	500	670	1.00

Table 3: Comparison of the storage stability at 50°C compared to the carrier oil

Compound	Storage time (h)	Wavelength (nm)	Extinction (normalized)
4	500	758	0.80
5	500	756	1.00
6	500	756	0.88
7	500	756	0.85
9	500	670	0.90

10 In the presence of carrier oil, the comparative compound exhibited a distinctly sharper decrease in the normalized extinction as a function of time than in the case of the presence of detergent. The values were therefore not reproduced.

15 B) The storage stability of compounds 10 to 12 compared to detergent and the fuel and lubricant additive concentrate from Table 1 was investigated. To this end, solutions having a content of 1% by weight of compounds 10 to 12 in the detergent or the fuel and lubricant additive concentrate were prepared and the normalized extinction was determined as a function of the storage time both at room temperature and at 40°C. The normalization was to the extinction value at

the start of storage (i.e. immediately after preparation of the appropriate solution).  
The results are listed hereinbelow.

Compound 10:

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Detergent at room temperature: after storage times of 7 and 14 days, no change could be detected in the normalized extinction.

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Detergent at 40°C: after storage times of 7 and 14 days, no change could be detected in the normalized extinction.

Fuel and lubricant additive concentrate at room temperature: after storage times of 7 and 14 days, no change could be detected in the normalized extinction.

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Fuel and lubricant additive concentrate at 40°C: after storage times of 7 and 14 days, no change could be detected in the normalized extinction.

Compound 11:

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Detergent at room temperature: after storage times of 4, 12, 28 and 42 days, no change could be detected in the normalized extinction.

Detergent at 40°C: after storage times of 4, 12, 28 and 42 days, no change could be detected in the normalized extinction.

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Fuel and lubricant additive concentrate at room temperature: after storage times of 21 and 28 days, no change in the normalized extinction could be detected.

Fuel and lubricant additive concentrate at 40°C: after storage times of 21 and 28 days, no change in the normalized extinction could be detected.

Compound 12:

- 5 Detergent at room temperature: after storage times of 4, 12, 28 and 42 days, substantially no change could be detected in the normalized extinction. The results are shown by the following table:

Storage time (days)	Extinction (normalized)
0	1.00
4	1.00
12	0.99
28	0.97
42	0.99

- 10 Detergent at 40°C: after storage times of 4, 12, 28 and 42 days, substantially no change could be detected in the normalized extinction. The results are shown by the following table:

Storage time (days)	Extinction (normalized)
0	1.00
4	1.00
12	0.99
28	0.98
42	0.98